

Tracing Chromium from Rock to Bay: Utilization of Stable Chromium Isotopes in Ecological and Human Water Systems

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Public Comments

No public comments were received for this proposal.

Initial Selection Panel Review

Proposal Title

#0109: Tracing Chromium from Rock to Bay: Utilization of Stable Chromium Isotopes in Ecological and Human Water Systems

Funding:

Do not fund

Initial Selection Panel (Primary) Review

Topic Areas

- Processes Controlling Delta Water Quality
- Assessment And Monitoring

Please describe the relevance and strategic importance of this proposal in the context of this PSP. How does the proposal address the topic areas identified above? What are the broader CALFED Goals this proposal may meet that are not accounted for in these specific topic areas?

Proposal No. 109 Tracing Chromium from Rock to Bay:
Utilization of Stable Chromium Isotopes in Ecological and
Human Water Systems The final technical panel rating for this
proposal was 'above average.' Apparently, a 'collaboration'
review was not performed. The proposal seeks Phase I funding
(\$1,200,000) to 'examine chromium cycling in the entire San
Francisco ecosystem.' Specifically, the team proposes to
collect Cr isotope data for a number of stream sites as a
baseline for Phase II studies and to 'couple' this data set
with laboratory work focused on answering two questions: (1)
how does the redox potential of Mn oxide-rich soil affect the
percentage of 'heavy' Cr atoms its pore water contains; and
(2) can naturally occurring organic acids create 'fractionated
Cr pools under equilibrium conditions?' The proposal suggests
that routinely or strategically measuring the percentage of
this rare, heavy species of Cr in a water sample might someday

#0109: Tracing Chromium from Rock to Bay: Utilization of Stable Chromium Iso...

Initial Selection Panel Review

help Calfed more accurately or precisely assess how much and from where 'toxic forms of Cr' arrive and exit through an aquifer or through the Delta. It also suggests that 'With a clearer Cr systematics, we may be able to begin to make crude predictions about the changes in trace metal delivery to fluvial and estuarine systems resulting from climatic and vegetative shifts.' Of the two types of proposed activities (field and lab), the field work has greater potential for directly addressing Calfed concerns about trace metal contamination of groundwater banks (or more precisely, 'CWUM-ARSS-conjunctive water use management-artificial recharge systems'). The stable isotope work may someday prove able to distinguish between Cr atoms leached from the weathering of chromium steel and atoms liberated from native serpentine soils. How well this nascent technique might perform as a biogeochemical tracer is unclear, however. The proponents offer hope with the observation that 'the stable isotopic composition of environmental samples has allowed tremendous insight into the origin, fate, and transport of macronutrients (e.g., C, N, O, S) through atmospheric and hydrologic cycles (see Kendall and McDonnell, 1998).' But Calfed-funded research so far (>\$2 million?) has revealed only that these lighter-than-Cr isotopes do not behave in the Bay-Delta as predictably as in the systems described in Kendall and McDonnell (1998). This proposal contained inconsistencies, omissions and exaggeration. Early in the proposal the proponents express the concentration of the 'toxic' form of Cr in nanomoles per liter (nM), e.g., 'a relatively constant Cr(VI) concentration (20 nM]'. To proclaim that 'The proposed research is fundamental to properly balancing and optimizing management of water operations and biological resources [of the Delta]' or to predict that 'CWUM will fundamentally alter California's water cycle' might strike some reviewers as bordering on hyperbole. The most glaring shortcoming of this proposal, however, may be its meager list of deliverables. After three years and \$1.2 million, Calfed might expect a more 'user-friendly' set of final products than an 'improved understanding of Cr systematics' and an 'interpretive report ready for colleague review.' Perhaps, this fault rests not so much with the applicants as on how narrow the 'Deliverables' column is on

Initial Selection Panel Review

the electronic application form.

The budgets of proposals submitted in response to this PSP are larger, on average, than those submitted to CALFED in previous years. The Science Program is committed to getting as much science per dollar as is reasonably possible. With this commitment in mind, can the proposed budget be streamlined? If so, please recommend and clearly justify a new budget total in the space provided.

The proposed project could be streamlined by eliminating most of the isotope work and initiating instead a three year campaign of strategic field studies whose main goal would be to quantify (even non-parametrically would do) the relative risk of trace metal contamination in a stratified random sample of potential CWUM-ARS sites. Most of the budget would thus be expended on nested catchment monitoring of trace metals (along with the standard suite of limnological variables) under low and especially high flow conditions and on tracer injection tracking studies for as many potential CWUM-ARS sites as practical. [Note: Reclamation could (for only the cost of fuel) make its 45-foot R/V Endeavor-with skipper available as safe and reliable platform for collecting trace metal samples along the axis of the Bay-Delta; check the Calfed Science Consortium web site]. The remainder of the funding would focus on 'mining' the NASQAN, NAWQA and GAMA historical data streams and making them available in an easy to use form via the Web. The revised scope would include a more fully developed list of deliverables and due dates. One deliverable would be a technical memorandum (with accompanying data, metadata and calculation spreadsheets) comparing trace metal composition and concentration in the Delta and its catchment to conditions in other parts of the country. Another deliverable would be an on-line Calfed Science Journal presentation of the study's major findings, including an estimate of the flow-weighted mean annual concentration of Cr(VI) at the head of the California Aqueduct (or some other location suitable for tracking the concentration of Cr in exported water) and a preliminary ranking of CWUM-ARS site vulnerability to toxic trace metal contamination.

Initial Selection Panel Review

Evaluation Summary And Rating.

Provide a brief explanation of your summary rating and any additional comments you feel are pertinent.

Selection Panel (Discussion) Review

fund this amount: \$0

note:

do not fund

The Panel acknowledged the potential importance of understanding chromium movement through the San Francisco Estuary. However, much of the study focuses on sophisticated laboratory explorations that are not necessarily germane to the management implications the proposal identified. These laboratory studies are not well-integrated with the field component of the study, which the Panel felt was more relevant to CalFed's management needs. The Panel did not feel that the proposal demonstrated that chromium contamination should be one of CalFed's top management concerns at this time.

Panel Ranking: Do not fund

Technical Synthesis Panel Review

Proposal Title

#0109: Tracing Chromium from Rock to Bay: Utilization of Stable Chromium Isotopes in Ecological and Human Water Systems

Final Panel Rating
above average

Technical Synthesis Panel (Primary) Review

TSP Primary Reviewer's Evaluation Summary And Rating:

Overall, this is a well constructed research plan for a very ambitious study of the geochemistry of chromium in the delta region, built upon the assumption that chromium VI will be a more significant water contaminant in future water management decisions as more data on its human and ecological risks is revealed. It is not certain that is the case, but it is a reasonable hypothesis to drive future research. The research builds on a considerable amount of information on chromium in the Bay-Delta system. One of the reviewers opines that "the major features of Cr behavior in SF Bay and the rivers coming into it are pretty well understood. For example, we know natural weathering of ultra-mafic rocks is a more important source than are human activities. Cr distribution patterns in the Bay are complex but there do not seem to be ecologically harmful amounts of Cr there." The authors propose, however, to generate new information through the use of stable chromium isotopes, expecting that this technique will provide new insights into the sources and distribution of chromium in the system; and on the role of manganese oxides, bacteria and organic carbon in the process. The team that has been assembled does not appear to have the appropriate credentials to carry out all of the work included in this ambitious plan, although there is a leading Cr isotope expert on the team. The

#0109: Tracing Chromium from Rock to Bay: Utilization of Stable Chromium Iso...

Technical Synthesis Panel Review

budget is large and one wonders if a smaller study that explores how Cr isotopes would be a wiser use of CALFED funds. Nonetheless the plan itself is well constructed and the budget is reasonable for the project as laid out. External reviewers expressed some concerns that the use of chromium isotopes for this purpose is yet unproven, making it unclear that the study will lead immediately to information that will inform Bay-Delta management any more than the data already available. The study does promise to yield some more information on some of the processes that are important in chromium transport that have not as yet been thoroughly investigated. It should also be noted that chromium levels in water exported from the Delta are certainly of concern to utilities downstream and so this study may have relevance in that arena.

Additional Comments:

The proposal assumes that chromium VI levels in exported water from the delta will be a subject of growing interest as health effects data on this species continue to be produced by the NTP and EPA. As one reviewer notes, there is the possibility that the levels of chromium in the Delta will not reach levels of significance to human or ecological health but who can be sure at this time what these levels will be. In any case, it is not out of the question that future management decisions will have to be made to curtail chromium levels in the entire system. So, more information on the relevant processes that determine residuals of Cr in the water column is a desirable goal. The proposing team have produced a strong, scientifically valid approach which should move this research agenda forward if the use of Cr isotope proves to be a transformative technique. If not, little will be achieved from this project that is not already known which is clearly a risk.

Overall, this is a well constructed research plan for a very ambitious study of the geochemistry of chromium in the delta region, built upon the assumption that chromium VI will be a more significant water contaminant in future water management decisions as more data on its human and ecological risks is

Technical Synthesis Panel Review

revealed. It is not certain that is the case, but it is a reasonable hypothesis to drive future research. The research builds on a considerable amount of information on chromium in the Bay-Delta system. One of the reviewers opines that "the major features of Cr behavior in SF Bay and the rivers coming into it are pretty well understood. For example, we know natural weathering of ultra-mafic rocks is a more important source than are human activities. Cr distribution patterns in the Bay are complex but there do not seem to be ecologically harmful amounts of Cr there." The authors propose, however, to generate new information through the use of stable chromium isotopes, expecting that this technique will provide new insights into the sources and distribution of chromium in the system; and on the role of manganese oxides, bacteria and organic carbon in the process. The team that has been assembled does not appear to have the appropriate credentials to carry out all of the work included in this ambitious plan, although there is a leading Cr isotope expert on the team. The budget is large and one wonders if a smaller study that explores how Cr isotopes would be a wiser use of CALFED funds. Nonetheless the plan itself is well constructed and the budget is reasonable for the project as laid out. External reviewers expressed some concerns that the use of chromium isotopes for this purpose is yet unproven, making it unclear that the study will lead immediately to information that will inform Bay-Delta management any more than the data already available. The study does promise to yield some more information on some of the processes that are important in chromium transport that have not as yet been thoroughly investigated. It should also be noted that chromium levels in water exported from the Delta are certainly of concern to utilities downstream and so this study may have relevance in that arena.

Technical Synthesis Panel (Discussion) Review

TSP Observations, Findings And Recommendations:

The panel agreed that this was an important topic and a well-documented research proposal. There is substantial background on the distribution of chromium in the Bay-Delta system; but little is known about the processes that are most

Technical Synthesis Panel Review

important in the movement of chromium through biological systems. The panel expressed concern that there may not be sufficient background information to allow successful completion. For example, the use of chromium isotopes is a new technique and a promising one; however, the panel wondered whether the techniques are developed enough to allow interpretation of the data to distinguish sources of chromium and details of transport/transformation processes.

Technical Review #1

proposal title: Tracing Chromium from Rock to Bay: Utilization of Stable Chromium Isotopes in Ecological and Human Water Systems

Review Form

Goals

Are the goals, objectives and hypotheses clearly stated and internally consistent? Is the idea timely and important?

Comments	<p>In this proposal, the PIs describe a comprehensive study of chromium (Cr) geochemistry throughout the San Francisco Bay ecosystem (including headwaters of the San Joaquin and Sacramento Rivers). The impetus for this project is that proposed "conjunctive water use management" (CWUM) may cause increased mobilization of Cr into the water supply. Cr in the hexavalent form can be toxic in the ppb concentration range. This is a multi-faceted proposal involving a) sampling of a wide variety of natural waters in the ecosystem for Cr, Cr chemical speciation, and Cr isotopes, b) characterization of microbial communities, c) studies of the effect of Cr oxidation by Mn oxides on Cr isotope fractionation, and d) investigation of the effect of low molecular weight organic acids (LMOA) on Cr speciation and solubilization.</p> <p>The goals, objectives, and hypotheses are clearly stated. If funded this project could certainly greatly advance our state of knowledge of low temperature Cr geochemistry. It is Task 1E (sampling of pilot artificial recharge systems) that is the most timely part of this project. If the PIs can't find significant (from a toxics point of view) Cr mobilization in these systems, then the justification for the rest of the project is moot. Why not do this task and the decide whether the rest of the work is justified?</p>
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Technical Review #1

Rating	very good
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Justification

Is the study justified relative to existing knowledge? Is a conceptual model clearly stated in the proposal and does it explain the underlying basis for the proposed work? Is the selection of research, pilot or demonstration project, or a full-scale implementation project justified?

Comments	<p>There could be better justification. The PIs present no data on what is known about Cr concentrations in this system nor is there more than speculative evidence provided as to what CWUM might do to Cr levels.</p> <p>Again, Task 1E is critical to justifying the whole project.</p>
Rating	good

Approach

Is the approach well designed and appropriate for meeting the objectives of the project? Is the approach feasible? Are results likely to add to the base of knowledge? Is the project likely to generate novel information, methodology, or approaches? Will the information ultimately be useful to decision makers?

Comments	<p>I have a number of questions and comments about the approach:</p> <p>1. In Task 1A, the PIs state they will "refine current ion exchange concentration and purification techniques." However, they offer not one word about what exactly they might do.</p> <p>2. In Task 1A, the PIs state that SF Bay waters "will serve as an endmember reflecting the integration of all Cr processes occurring throughout the watershed." However, it is far more likely these brackish bay samples will reflect bay processes rather than</p>
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Technical Review #1

	<p>watershed processes.</p> <p>3. In Task 1B, the PIs propose characterizing microbial communities in headwaters using PLFA analysis. However, nowhere do they show how this information will be or can be tied back to Cr speciation, fractionation, and mobilization.</p> <p>4. Task 2 (Cr isotope fractionation by Mn oxides) is potentially good basic science, but the approach needs to be described more fully. How do the experimental Mn oxides relate to what is in the environment? Will the levels of Cr used in the experiments be similar to natural levels? Why do the PIs think that LMOAs "may result in a surprising Cr(VI) fractionation signature"?</p> <p>5. Task 3A (CE analysis of Cr-LMOA complexes) is again interesting basic science. However, the PIs fail to specify what they mean by LMOAs---it seems like this just refers to simple organic acids like oxalate. Why do the PIs discount complexation by humics? This also seems to be a very major sub-project on its own. But here again detail is lacking.</p> <p>6. Task 3B (dissolution of Cr-phases by LMOAs) seems to refer to dissolution of Cr (hydr)oxides. Why do the PIs think that there are Cr solids in watershed sediments rather than Cr sorbed to or co-precipitated with other solid phases?</p>
Rating	very good

Feasibility

Is the approach fully documented and technically feasible? What is the likelihood of success?
Is the scale of the project consistent with the objectives and within the grasp of authors?

Comments	The project is generally feasible, with the caveats mentioned above under "approach." However, it does seem like a lot of work. Some of the sub-tasks (like
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Technical Review #1

	the work on Cr-organic complexation) are major efforts in and of themselves.
Rating	very good

Monitoring

If applicable, is monitoring appropriately designed (pre–post comparisons; treatment–control comparisons)? Are there plans to interpret monitoring data or otherwise develop information?

Comments	N/A
Rating	not applicable

Products

Are products of value likely from the project? Are contributions to larger data management systems relevant and considered? Are interpretive (or interpretable) outcomes likely from the project?

Comments	If they accomplish all that they propose, the PIs will provide a lot of very interesting and potentially useful research on Cr geochemistry both from a specific watershed point of view as well as from a fundamental research prospective.
Rating	very good

Additional Comments

Comments

Capabilities

What is the track record of authors in terms of past performance? Is the project team qualified to efficiently and effectively implement the proposed project? Do they have available the infrastructure and other aspects of support necessary to accomplish the project?

Comments	This is an impressive group of PIs with strong track records and the available facilities to accomplish
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Technical Review #1

	this work. These people can get the job done and produce top-quality publishable science.
Rating	excellent

Budget

Is the budget reasonable and adequate for the work proposed?

Comments	The budget is breath-taking, but then again so is the scope of work.
Rating	very good

Overall

Provide a brief explanation of your summary rating.

Comments	This is a very comprehensive approach to studying Cr mobilization and transport in a watershed. It would undoubtedly result in some interesting and useful advances in our understanding of the geochemistry of this potentially toxic element. However, many of the details of the approach are missing. Furthermore, the stated justification for the project would suggest that Task 1E needs to be accomplished before there is a true justification for the rest of the project in the context of this program.
Rating	very good

Technical Review #2

proposal title: Tracing Chromium from Rock to Bay: Utilization of Stable Chromium Isotopes in Ecological and Human Water Systems

Review Form

Goals

Are the goals, objectives and hypotheses clearly stated and internally consistent? Is the idea timely and important?

Comments	The PIs have framed the goals and hypotheses very broadly, which is generally consistent with the state of our knowledge at this point in time. In certain areas however, I believe they could have done a better job in taking existing data and formulating testable hypotheses. Certainly conjunctive use of water needs to be examined VERY carefully before implementation, and IF the potential for significant Cr contamination exists (which is rather poorly documented in the proposal), then the idea is definitely timely and important. Some of the analytical science may not be ready for implementation as described in the proposal.
Rating	good

Justification

Is the study justified relative to existing knowledge? Is a conceptual model clearly stated in the proposal and does it explain the underlying basis for the proposed work? Is the selection of research, pilot or demonstration project, or a full-scale implementation project justified?

Comments	The PI's have not made a convincing case that the toxic species of Cr (Cr(VI)) is an emerging threat to human health. Few data
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Technical Review #2

are presented to justify this tenet - in fact if anything the data that is referenced indicates the opposite. Ecosystem perturbations are harder to demonstrate/document but the potential for impact is there. However the case is not made (via toxicological citations, etc.) that current or projected Cr levels pose an ecosystem threat. Cr(III) species have low solubility in most aqueous environments and are relatively immobile, while Cr(VI) is certainly more mobile and soluble, and in higher organisms toxic, its effect on lower trophic levels at typical environmental levels is likely minimal. Again, the proposal could have been much stronger by referencing studies demonstrating effects of elevated Cr levels on specific components of aquatic food chains. While systemic, widespread impacts are unlikely, it is conceivable that localized perturbations will occur (e.g. in ARS's) and if the proposed work is to proceed I would recommend scaling back to pilot studies in one of these areas.

A significant deficiency in the proposal is the lack of any Cr isotope data (preliminary or otherwise) that would back the PI's assertion that isotope fractionation data will provide valuable information on Cr sourcing and flow-path processing mechanisms in the context of CWUM/ARC concerns. Some relevant site-specific data should be presented to justify a project of this scale.

Despite what the authors intimate, I'm not aware of a single study that has distinguished anthropogenic environmental pools of Cr, from geologic ones, by using

Technical Review #2

	Cr isotopic signatures. The applied environmental application of isotope fractionation of "heavy elements" is still very much in its infancy - the basic fractionation process studies should and must proceed, but large scale application to environmental issues is premature.
Rating	good

Approach

Is the approach well designed and appropriate for meeting the objectives of the project? Is the approach feasible? Are results likely to add to the base of knowledge? Is the project likely to generate novel information, methodology, or approaches? Will the information ultimately be useful to decision makers?

Comments	<p>It is clear from the proposal narrative that the proposal authors have a good understanding of Cr chemistry, particularly the details of its coordination chemistry. Chromium biochemistry/biology has essentially been totally ignored, but the scope is already too large.</p> <p>The design of the field component of the proposal is poorly conceived and disjointed. The scope is overly broad with critical details missing, and ultimately self-defeating. The authors are certainly aware of the relevant environmental pools and bridging mechanism, but as presented, the field sampling effort does not effectively put them together. Each pool deserves a more concerted effort.</p> <p>More emphasis should be placed on the III/VI measurements and relevant sampling bias, preservation, transformation issues. Hexchrome is the primary issue and unequivocal VI data is what is needed</p>
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Technical Review #2

first. Much, if not all, of the most relevant management issues can be addressed with oxidation state speciation (i.e. without isotope ratio measurements).

It not clear from the narrative that the time scales of the fractionation and dissolution processes discussed for Cr, have relevance to that experienced in CWUM/ARC. They may be, but the authors could press their case better if they were to discuss the hydrogeologic residence times.

From an analytical viewpoint, the capillary electrophoresis studies are elegant and well suited to address some fundamental questions concerning organic-acid enhanced dissolution of chromium-containing minerals. This work is important and will add substantially to our general understanding of dissolution processes. Its obvious that an improved understanding of DOC-trace element interactions are key to more predictive modeling of trace element speciation, transport, and bioavailability. However, it's not clear that this effort will have sufficient relevance or payoff for the short-term applied goals of the CALFED program. "Fingerprinting" specific ligand-mobilized Cr species (as the authors' remark) is hyperbole for some time to come. Identification of Cr-ligand species in the complex milieu of natural organic matter is quite different than pure compound lab studies. Mass spectrometry tools will need to be better integrated.

A better focus on Cr(III) mineralogy in natural environments is needed (reaction rates are critically dependent upon the

Technical Review #2

	<p>solid phase chemistry) - especially in comparison with synthetic phases prepared in the laboratory.</p> <p>The PLFA work is also intriguing and has real potential to get at metal-specific biotic interactions. Again, however, the tool needs further environmental grounding before applying to the issues under consideration here. The authors are straying somewhat from the basic environmental issue that they set-up.</p> <p>Groundwater needs a stronger focus - sampling along extensive contiguous flowpaths would provide valuable information. The well sampling program as described is rather shotgun, though some valuable geochemical correlative information might result.</p> <p>I have not seen reliable isotope fractionation data for Cr coming from the multi-collector ICP-MS technique mentioned briefly in the proposal. The double-spike TIMS approach is capable of high quality fractionation data.</p> <p>A pilot scale project focused on a couple ARCs would be a more effective use of resources.</p>
Rating	very good

Feasibility

Is the approach fully documented and technically feasible? What is the likelihood of success?
Is the scale of the project consistent with the objectives and within the grasp of authors?

Comments	Laboratory studies suggest that Mn oxidation state and mineralogy are critical factors determining Cr isotope
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Technical Review #2

	<p>fraction. Environmental Mn speciation is obviously a lot more complex than in these lab studies and will likely never be sufficiently characterized to serve as a reliable variable input to address environmental Cr redox speciation/isotope fractionation. Similarly for pH, ionic strength and other oxidants along groundwater flow paths. The PI's acknowledge that the mechanisms underlying these redox reactions are complicated and messy even in "controlled" laboratory experiments.</p> <p>The PI's mention, to their credit, that adapting existing hexchrome selective ion-exchange methods to variable salinity environments will be necessary and critical. This could become more of a method development project than expected.</p> <p>Biannual or even quarterly sampling, while adequate for snapshots of speciation, are not sufficient to capture variability in event or even seasonally driven systems (e.g. soil flushing, stream discharge, etc.). Metal export yields or functions are unlikely to be sufficiently accurate with this limited sampling. This all requires major resources to accomplish and the field program as described is too broad to properly address any individual compartment.</p> <p>The authors have not addressed how they will speciate Cr on solid phases (suspended sediments and sediments). How will Cr be extracted for oxidation state measurements? Are you using XANES?</p>
Rating	good

Monitoring

If applicable, is monitoring appropriately designed (pre-post comparisons; treatment-control comparisons)? Are there plans to interpret monitoring data or otherwise develop information?

Comments	The project should not be considered a traditional monitoring program.
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Technical Review #2

Rating	not applicable
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Products

Are products of value likely from the project? Are contributions to larger data management systems relevant and considered? Are interpretive (or interpretable) outcomes likely from the project?

Comments	I suspect valuable contributions to our understanding of chromium mineral geochemistry will result from the controlled laboratory studies. I'm less convinced that will be the case with the field assessment component. A refocused and scaled-back effort would better target the immediate concerns of CWUM/ARS and Cr, and produce a product that would identify specific areas for future research. Assuming the technical issues with Cr(VI) isolation and quantification are overcome, it seems likely that the study, even as presently conceived, will produce useful data on levels of the two dominant oxidation state species of Cr.
Rating	good

Additional Comments

Comments	no additional comments
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Capabilities

What is the track record of authors in terms of past performance? Is the project team qualified to efficiently and effectively implement the proposed project? Do they have available the infrastructure and other aspects of support necessary to accomplish the project?

Comments	Project PI is one of the few experts in the world in the area of transition metal stable isotope fractionation. Despite this, only a couple peer-reviewed papers have been produced on Cr-isotope fractionation in nature. The underlying mechanisms are very complex and if an analogy can be made to Fe-isotope fractionation, the field of Cr-isotope
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Technical Review #2

	<p>fractionation is very clearly in its infancy. Despite over 100 scientists working in the much more mature field of Fe isotope fractionation (with strong parallels to Cr isotope work), environmental applications are really unproven. The assembled team of scientists appear to be top notch with considerable experience in the inorganic and geo-chemistry of Cr. A good mix of experienced senior researchers, young scientists and graduate/undergraduate students.</p>
Rating	very good

Budget

Is the budget reasonable and adequate for the work proposed?

Comments	<p>The budget is very large (nearly \$1.2 million), though given the scope of the proposal, commensurate with the tasks outlined. I do not believe, however, that the design and scale of the field effort is appropriate at this stage of applied Cr geochemistry. Overhead rates in the range of 55-60% are excessive.</p>
Rating	good

Overall

Provide a brief explanation of your summary rating.

Comments	<p>The science and understanding behind stable isotope fractionation of Cr must first be significantly improved/developed before it can be applied to a large scale field project such as proposed here, especially in the context of management options for conjunctive water use. The added value and expense of the isotope work beyond that of measurements of levels and oxidation state of Cr do not appear to be justified at this point. I do not disagree that fundamental work on low-temperature biogeochemical mechanisms of Cr isotope fractionation should be pursued.</p>
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Technical Review #2

	In contrast to the large and rather disjointed field plan presented, much more could be learned by designing and implementing a comprehensive study of the hydrology and geochemistry of a single ARS. Even in this context, I suspect good data on the levels and oxidation state of Cr species (without isotope data) could answer the most critical management issues.
Rating	very good

Technical Review #3

proposal title: Tracing Chromium from Rock to Bay: Utilization of Stable Chromium Isotopes in Ecological and Human Water Systems

Review Form

Goals

Are the goals, objectives and hypotheses clearly stated and internally consistent? Is the idea timely and important?

Comments	The authors propose to test a number of hypotheses so this large-budget proposal is broken down by task and sub-task. The hypotheses for each task are clearly stated. The ideas presented and tasks proposed are all interesting and while they are somewhat closely connected it would not be necessary to do everything to have a successful project.
Rating	very good

Justification

Is the study justified relative to existing knowledge? Is a conceptual model clearly stated in the proposal and does it explain the underlying basis for the proposed work? Is the selection of research, pilot or demonstration project, or a full-scale implementation project justified?

Comments	This proposal is aimed at a better understanding of Cr behavior in SF Bay and its watershed. Work done by Russ Flegal and others for the SF Bay Regional Monitoring Program and other programs has produced abundant data and modelling on this subject. The work proposed here will probably add to our understanding but I don't expect it to radically change what we now know.
Rating	

Technical Review #3

	good
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Approach

Is the approach well designed and appropriate for meeting the objectives of the project? Is the approach feasible? Are results likely to add to the base of knowledge? Is the project likely to generate novel information, methodology, or approaches? Will the information ultimately be useful to decision makers?

Comments	The heart of this proposed work is the use of Cr isotopes to help understand Cr behavior. This is a very new approach that has been used only a few times so far. It has the potential to be useful but has not made a major impact at this time. A lot of other measurements are also proposed, everything from other trace and major metals to organic acids to bacteria. Each of these potentially adds something useful but results in a very big budget. Maybe they should just focus on Cr. Even then, I'm not sure the data will be immediately usefull to resource managers.
Rating	very good

Feasibility

Is the approach fully documented and technically feasible? What is the likelihood of success? Is the scale of the project consistent with the objectives and within the grasp of authors?

Comments	Tom Bullen, one of the proposed PIs for this project, is the world's leading expert on Cr isotopes and a very competent scientist. If funded, he will produce something useful. The other PIs are also good scientists and can probably do what they propose, even though technical details are sketchy for some of the plans.
Rating	excellent

Technical Review #3

Monitoring

If applicable, is monitoring appropriately designed (pre–post comparisons; treatment–control comparisons)? Are there plans to interpret monitoring data or otherwise develop information?

Comments	They plan to sample 4 times a year over a two or three year period but this is not really a monitoring program and I'm not sure they need this much sampling.
Rating	good

Products

Are products of value likely from the project? Are contributions to larger data management systems relevant and considered? Are interpretive (or interpretable) outcomes likely from the project?

Comments	There will certainly be products of value from a scientific knowledge perspective. As I said before, I'm not sure this knowledge will lead to any short-term management changes. It's pretty clear from existing data that there is not a Cr pollution problem in SF Bay. The authors talk a lot about plans for storing captured rainwater in aquifers and how this might increase Cr pollution. I doubt that this would happen but even if it did, it's easy to treat the water to reduce Cr VI to Cr III and solve the problem.
Rating	very good

Additional Comments

Comments	The use of Cr isotopes is new, very innovative and potentially useful but is unlikely to result in easy to interpret data that radically changes our ideas on how Cr behaves in the study area. Some of the other things proposed, like how organic acids, bacteria and Mn oxides affect Cr behavior have been studied by others. What is proposed here is to see how they affect Cr isotope fractionation. The effects are
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Technical Review #3

	almost certain to be complex.
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Capabilities

What is the track record of authors in terms of past performance? Is the project team qualified to efficiently and effectively implement the proposed project? Do they have available the infrastructure and other aspects of support necessary to accomplish the project?

Comments	My impression is that all the authors are very good scientists who have access to first rate facilities.
Rating	excellent

Budget

Is the budget reasonable and adequate for the work proposed?

Comments	The budget is very high, mostly due to the large amounts of time put in by the PIs and the numerous tasks proposed. It should certainly be adequate.
Rating	good

Overall

Provide a brief explanation of your summary rating.

Comments	I think the major features of Cr behavior in SF Bay and the rivers coming into it are pretty well understood. For example, we know natural weathering of ultra-mafic rocks is a more important source than are human activities. Cr distribution patterns in the Bay are complex but there do not seem to be ecologically harmful amounts of Cr there. The use of Cr isotopes to better understand distributions and behavior is new, very innovative and potentially useful but is unlikely to result in easy to interpret data that radically changes our ideas on how Cr behaves in the study area. Some of the other things proposed, like how organic acids, bacteria and Mn oxides affect Cr isotope
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Technical Review #3

	fractionation are scientifically interesting.
Rating	very good

